Isochoric Heat Capacities of Pure Alcohols and Their Aqueous Mixtures

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Alcohol and water are highly polar molecules, and associate by hydrogen bonding in solution. Hydrogen bonding of molecules is certain to introduce an effect of the molecular energy to the heat capacity. Due to the presence of strong hydrogen bonding, interactions between water and alcohol molecules show anomalous thermodynamic properties. Measurements of thermodynamic properties are essential to characterize such interactions and to model this behavior with an equation of state. In order to develop a reliable equation of state for a fluid, various thermodynamic property measurements of the fluid are required. Among them, isochoric specific heat capacity measurements provide a very useful check for calculations of the second derivative of the pressure with respect to temperature, which is essential information to develop but is challenging to measure accurately.

Isochoric heat capacity of C1-C3 alcohols and binary mixtures of water with methanol, ethanol, and 1-propanol in the liquid phase have been measured in a temperatures range from 280 to 420 K, and at pressures up to 30 MPa. The measurements were carried out with a twin-cell type adiabatic calorimeter. Temperatures were measured with a platinum resistance thermometer on the bottom of each cell and were reported on the ITS-90. Sample pressure measurements were made with a quartz crystal transducer. Densities were calculated from the volume of the calorimeter cell and sample mass. The experimental expanded uncertainty (with a coverage factor k=2) of temperature measurements is 13 mK, and that of pressure measurement is 8 kPa. The expanded relative uncertainty for isochoric heat capacity is estimated to be 2 % for liquid phase measurements, and for density it is 0.16 %.